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The effects of physicochemical wastewater treatment operations on forward osmosis

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Abstract

Raw municipal wastewater from a full-scale wastewater treatment plant was physicochemically pre-treated in a large pilot-scale system comprising coagulation, flocculation, microsieving and microfiltration operated in various configurations. The produced microsieving filtrates and microfiltration permeates were then concentrated using forward osmosis (FO). Aquaporin Inside™ FO membranes were used for both the microsieving filtrate and microfiltration permeates, and HTI-TFC membranes for the microfiltration permeate using only NaCl as the draw solution. The FO performance was evaluated in terms of the water flux, water flux decline and solute rejections of biochemical oxygen demand and total and soluble phosphorus. The obtained results were compared with the results of forward osmosis after only mechanical pre-treatment. The FO permeates satisfied the Swedish discharge demands for small and medium-sized wastewater treatment plants. The study demonstrates that physicochemical pre-treatment can improve the FO water flux by up to 20%. In contrast, the solute rejection decreases significantly compared to the FO-treated wastewater with mechanical pre-treatment.

Key words: Forward osmosis, non-biological treatment, microfiltration, microsieving, physicochemical pre-treatment, wastewater treatment

Introduction

The need to recover valuable resources from wastewater has been emphasized over the past 20 years, in which the direct utilization of nutrients from municipal wastewater has been described as (direct) sewer mining [1-3]. Membrane technologies such as microfiltration (MF) and ultrafiltration (UF) have proven to be successful separation techniques to produce on-demand nutrient-rich water that is free of particles and pathogens and hence suitable for irrigation [4].

The concept of municipal wastewater treatment using membrane filtration without biological treatment steps has been referred to as direct membrane filtration, direct membrane separation and direct sewage microfiltration [5-7]. The direct membrane filtration (DMF) concept has been tested on different wastewater types, such as raw municipal wastewater, primary settler effluent, domestic wastewater from an apartment and a dormitory complex and grey water [5-13]. However, as the DMF concept only retains particles and bacteria, the reported permeate quality did not satisfy the present Swedish wastewater discharge demands for small and medium-sized wastewater treatment plants (WWTPs) because the soluble carbon and phosphorus (and nitrogen) are not retained. By combining DMF with physicochemical pre-treatments, such as coagulation and flocculation, it is possible to meet the wastewater discharge demands, as shown in the pilot-scale study by Hey et al. [14], requiring 0.4 kWh·m⁻³ treated wastewater. However, if higher levels of removal are required, more advanced techniques must be added to the wastewater treatment process. The same study also showed a significant improvement in the MF permeate flux by 20% in comparison to mechanical pre-treatment only, i.e., microsieving (MS) and MF.

In addition to the non-biological DMF concept, the forward osmosis (FO) membrane process has been suggested as a promising technology with the ability to concentrate wastewater [2-3,15] with high retentions of biochemical oxygen demand [16], chemical oxygen demand [15] and total and soluble phosphorus [15-16]. In comparison to a pressure-driven membrane process, e.g., MF, the FO process operates at a non-hydraulic pressure, utilizing the osmotic pressure difference across a semi-permeable FO membrane placed between a feed solution of low osmotic pressure and a draw solution of high osmotic pressure [15]. Because the FO process naturally attempts to achieve an osmotic equilibrium, water moves from the feed solution to the draw solution across the FO membrane, reducing the draw solution's osmotic potential [17]. The reported advantages of FO over pressure-driven membrane processes include its lower fouling propensity [18], high water flux recovery [17], high rejection of a wide range of trace organic compounds [19-21] and heavy metals [22] and reduced capital and operational costs [18]. FO membrane studies have been performed with different wastewater types, such as municipal wastewater and synthetic wastewater [15-16,18,22-27].

Few studies have reported the effects of using different pre-treatment methods, e.g., mechanical [16] and physicochemical, before FO. In fact, the FO process is mostly considered as a pre-treatment step to concentrate wastewater [28]. Coday et al. [21] suggested coagulation, flocculation or MF as suitable pre-treatment methods before FO, while Lutchmiah et al. [29] argued that extensive pre-treatment systems for FO may be redundant when treating complex feeds, depending on the FO membrane

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70 performance. However, the amount of publications considering physicochemical pre-treatment of
71 municipal wastewater before FO is limited..

72 In contrast, several studies have been conducted by treating water or wastewater with coagulation
73 and/or flocculation as a pre-treatment to pressure-driven membrane (MF or UF) processes to prevent
74 fouling [30-31]. Coagulation has been found to be the most successful pre-treatment for fouling
75 reduction on thin film composite (RO-TFC) membranes, reducing the dissolved organic carbon (DOC),
76 which is an important fouling factor, by 30%. Furthermore, coagulated flocs can deposit on the
77 membrane surface and act as protection for the membrane, whereas the cake layer can easily be
78 removed. However, a proper dosage of coagulant and flocculant prevents membrane fouling and can
79 enhance membrane performance, whereas overdosing by a small amount, e.g., 50 ppb of Al^{3+} , can
80 foul the membrane [32]. Furthermore, insoluble coagulants can form preflocs that attach to any
81 surface and neutralize its charge. For flocculation, polyacrylamide polymer can cause membrane
82 damage by covering the polyamide surface, which can be prevented by accounting for the molecular
83 weight, charge density, solubility and charge position. Furthermore, anionic charged polymers have
84 been shown to be better at removing organic and cationic compounds compared to cationic charged
85 polymers, enhancing the MF water flux [14,32].

86 The scope of this study is to ascertain the effects of the physicochemical pre-treatment of municipal
87 wastewater before FO, including coagulation, flocculation (anionic- or cationic-charged
88 polyacrylamide-based polymer), microsieving and microfiltration. The produced feed types from a pilot-
89 scale setup were tested on two different thin-film composite (TFC) FO membranes, and the
90 performance was characterized in terms of the water flux, water flux decrease and solute rejection.
91 The membranes were not compared with respect to reverse salt flux and concentration polarization
92 effects. Furthermore, the achieved results were evaluated and compared with the FO results from
93 wastewater with only mechanical pre-treatment [16]. The final concentrations of the biochemical
94 oxygen demand (BOD_7) and the total and soluble phosphorus (TPt and TPs) in the FO permeate were
95 evaluated to meet the Swedish discharge demands for small and medium-sized WWTPs (BOD_7
96 $15\text{ mg}\cdot\text{L}^{-1}$ and TPt $0.5\text{ mg}\cdot\text{L}^{-1}$).

97 **Materials and Methods**

98 At the Källby WWTP, Lund, Sweden, the incoming wastewater is of medium strength (see Table 2)
99 according to the criteria described by Tchobanoglous et al. [33]. The wastewater is treated with 6-mm
100 perforated hole-plate bar screens (EscaMax, Huber AG, Germany) with subsequent sand removal in a
101 sand trap. The internal streams occurring at the WWTP, i.e., centrate water from the anaerobic
102 digester and chemically precipitated sludge from the tertiary treatment step (P removal with $FeCl_3$), are
103 released before the sand trap (see Figure 1). Because the screen and the sand trap are part of the
104 mechanical treatment steps in WWTPs [33], the term pre-treatment in this study is defined as the
105 treatment methods applied between the sand trap outlet and forward osmosis. Aquaporin Inside™
106 (Aquaporin A/S, Denmark) and Hydration Technologies Inc. (Albany, OR, USA) FO membranes are
107 henceforth referred to as AIM and HTI, respectively.

To test the effect of the different physicochemical pre-treatment configurations before FO (see Figure 1 and Table 1), a pilot-scale plant was constructed. The feed to the pilot-scale plant was taken at the sand trap outlet (Raw), where the coagulation and flocculation were followed by mechanical pre-treatment steps that included MS followed by MF. Each treatment configuration, as presented in Table 1, was operated for more than 6 days to ensure stable MF operation before a grab sample was obtained to be subjected to forward osmosis [14]. Furthermore, each grab sample, e.g., microsieve filtrate (MSF) and microfiltration permeate (MFP), was collected at different points.

A schematic of the pilot-scale plant is shown in Figure 1. The upper treatment path is described as MS, including only the microsieve, and the MSF is used as a feed solution for the AIM (MSF-AIM). The lower treatment path, described as MS+MF, includes MS and MF, where the produced MF permeate (MFP) is used as the feed solution for both the AIM (MFP-AIM) and HTI (MFP-HTI) FO membranes. The black dots in Figure 1 represent the sampling points at the sand trap outlet (Raw), MSF and MFP.

Coagulation and flocculation

Coagulation and flocculation were performed with the coagulant and/or flocculant added proportionally ($\text{L}\cdot\text{m}^{-3}$) to the feed before entering the respective mixing tanks. In the coagulation step, polyaluminum chloride (PACl; Kemira, Sweden) was used to reach a final concentration of $15\text{ mg}\cdot\text{L}^{-1}$ in the feed and mixed with a velocity gradient (G-value) of $100\text{--}200\text{ s}^{-1}$. For flocculation, either anionically or cationically charged polyacrylamide-based polymers (Veolia, France) were used. The flocculant was dosed in the same manner as the coagulant to a final feed concentration of $3\text{ mg}\cdot\text{L}^{-1}$ (anionic polymer) or $4\text{ mg}\cdot\text{L}^{-1}$ (cationic polymer) with a G-value of $80\text{--}150\text{ s}^{-1}$. The coagulation and flocculation structure was identical to that described in Väänänen et al. [34].

Microsieve

A drum rotating microsieve (HDF801-1H, Hydrotech AB, Sweden) with a total filter area of 0.33 m^2 and pore openings of $100\text{ }\mu\text{m}$ was operated at $2.0\text{ m}^3\cdot\text{h}^{-1}$. The produced microsieve filtrate was either used directly as the feed solution for FO (MS treatment path) or as the feed for microfiltration (MS+MF treatment path), as shown in Figure 1. The operational principle of the microsieve filter is described in Ljunggren et al. [35], and the operation, including the filter cloth cleaning, is described in Remy et al. [36] and Väänänen et al. [34].

Microfiltration

MF was performed with five flat-sheet membranes (MFP2, Alfa Laval A/S, Denmark) assembled in a plate and frame module, resulting in a 1.025 m^2 effective membrane area with a nominal pore size of $0.2\text{ }\mu\text{m}$. The microsieve filtrate was always used as the feed for the MF, as shown in Figure 1. The MF was operated in outside-in mode at a constant hydrostatic pressure of 3 kPa (0.03 bar), which was induced by the feed level over the membrane. Permeate was produced in 10-min cycles, each followed by 2 min of membrane relaxation with no back-flushing during operation, similar to the method described by Abdessemed et al. [9]. Scouring air was continuously supplied from the bottom of the membrane module with a specific air demand of $0.69\text{ Nm}^3\cdot\text{m}^{-2}\cdot\text{h}^{-1}$, which was controlled by an

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3 145 air flow meter. The hydraulic retention time in the MF tank was less than 6 min to avoid biological
4 146 activity in the tank. A more detailed description of the pilot-scale plant setup and the conducted
5 147 experiments can be found in Hey et al. [14].
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8 148 **Forward osmosis**
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10 149 **Forward osmosis membranes**
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12 150 FO experiments were conducted with two types of flat-sheet TFC FO membranes: AIM (from
13 151 Aquaporin A/S, Denmark) and HTI (from Hydration Technology Innovations, Albany, OR, USA). The
14 152 AIM membrane is a modified TFC membrane with an active layer (AL) containing biomimetic
15 153 aquaporin proteins reconstituted in spherical vesicles encapsulated by a polyamide thin film supported
16 154 by polyethersulphone (PES) [37]. The HTI TFC membrane is prepared using polyamide embedded on
17 155 a polysulfone support [38].
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21 156 **Experimental overview**
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23 157 The microfiltration permeate feed types were tested with AIM and HTI membranes, whereas the
24 158 microsieve filtrate feed was only tested with the AIM membrane because the HTI membranes were no
25 159 longer available from the supplier. Table 1 shows the different pilot-scale pre-treatment configurations,
26 160 producing FO feed that then was used in the AIM and HTI membrane experiments.
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29 161 **Liquid sampling and analysis**
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31 162 Depending on the experiment, MS (upper treatment path in Figure 1) or MS+MF (lower treatment path
32 163 in Figure 1) grab samples were collected at the sampling points (Raw, MSF and MFP) shown as black
33 164 dots in Figure 1. The samples were also obtained from the feed solution and draw solution before and
34 165 after each FO experiment. Standard methods were used for analysing the suspended solids (SS,
35 166 ISO 11923:1997), BOD₇ (ISO 5815-1;2:2003), TPt and TPs (ISO 6878:2004).
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38 167 **Forward osmosis experimental configuration**
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40 168 Two identical configurations were installed to conduct experiments in parallel with the AIM and HTI
41 169 membranes. Each configuration comprised a rectangular membrane module with a membrane
42 170 separating two identical compartments, each with dimensions of 175 mm (length), 80 mm (width) and
43 171 1.3 mm (height). The active tested membrane area was 140 cm². Both the AIM and HTI membranes
44 172 were tested with the active layer (AL) facing the feed solution (FS), denoted as AL-FS mode. A mesh
45 173 spacer with a thickness of 1 mm was placed on the support side of the membrane. A flow rate of
46 174 260 mL·min⁻¹ was used, generating a cross-flow velocity (u_{cr}) of 4.17 cm·s⁻¹, and the counter-current
47 175 circulation of the feed and draw solutions was created by two micro-gear pumps (WT3000-1JB/M,
48 176 Longer Pump, China) connected with Tygon®-tubing (R-3603, Saint-Gobain Performance Plastics
49 177 France – Site de Charny, France).
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55 178 The draw solution (2 M NaCl) and feed solution were kept in 5-L reservoirs with a volume of 2 L at the
56 179 beginning of each FO experiment. During the experiment, the mass change of the draw solution was
57 180 measured with an electronic balance (FKB36K0.1, Kern & Sohn GmbH, Germany) sampled every 5
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minutes. All experiments were conducted at room temperature, $20^{\circ}\text{C} \pm 2^{\circ}\text{C}$. A schematic of the laboratory FO setup is shown in Figure 2. The duration of each experiment was 4.5 h.

Quantification of water flux, water flux decrease, solute concentration and rejection

The average water flux (J_W , $\text{L} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$) was determined using an electronic balance, monitoring the rate at which the weight of the draw solution increased:

$$J_W = \frac{V_{\text{Permeate}}}{A_m \cdot \Delta t} \quad (\text{Eq. 1})$$

where V_{Permeate} (L) is the permeate volume during the experiment, which is defined as the difference between the final volume of the draw solution ($V_{\text{Draw}(t = \text{End})}$, L) and the initial volume of the draw solution ($V_{\text{Draw}(t = 0)}$, L). A_m (m^2) is the effective FO membrane surface area (0.014 m^2), and Δt (h) is the experimental time duration.

The water flux decrease ($J_{W,\%}$, %) was calculated without accounting for the dilution of the draw solution:

$$J_{W,\%} = \frac{J_W(t=0) - J_W(t=\text{End})}{J_W(t=0)} \quad (\text{Eq. 2})$$

where $J_{W(t=0)}$ ($\text{L} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$) is the initial water flux, and $J_{W(t=\text{End})}$ ($\text{L} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$) is the final water flux.

To evaluate the quality of the produced FO permeate, the final concentrations (C_{Permeate} , $\text{mg} \cdot \text{L}^{-1}$) of BOD_7 , TPT and TPs were calculated,

$$C_{\text{Permeate}} = \frac{V_{\text{Draw}(t=\text{End})} \cdot C_{\text{Draw}(t=\text{End})} - V_{\text{Draw}(t=0)} \cdot C_{\text{Draw}(t=0)}}{V_{\text{Permeate}}} \quad (\text{Eq. 3})$$

where $V_{\text{Draw}(t=\text{End})}$ (L) is the final volume and $C_{\text{Draw}(t=\text{End})}$ ($\text{mg} \cdot \text{L}^{-1}$) is the final concentration in the draw solution, $V_{\text{Draw}(t=0)}$ (L) is the initial volume and $C_{\text{Draw}(t=0)}$ ($\text{mg} \cdot \text{L}^{-1}$) is the initial concentration in the draw solution, and V_{Permeate} (L) is the permeate volume during the experiment, which is defined as the difference between the final volume of the draw solution ($V_{\text{Draw}(t=\text{End})}$, L) and the initial volume of the draw solution ($V_{\text{Draw}(t=0)}$, L).

The solute rejection (R, %) was calculated as follows:

$$R (\%) = 1 - \frac{C_{\text{Permeate}}}{C_{\text{Feed(Avg)}}} \cdot 100\% \quad (\text{Eq. 4})$$

where R (%) is the solute rejection, C_{Permeate} ($\text{mg} \cdot \text{L}^{-1}$) is the concentration in the permeate, and $C_{\text{Feed(Avg.)}}$ ($\text{mg} \cdot \text{L}^{-1}$) is the average concentration in the FS during the experiment; see Liu et al. [20] for further details.

The average concentration in the feed solution was calculated as follows:

$$C_{\text{Feed(Avg.)}} = \frac{C_{\text{Feed}(t=0)} + C_{\text{Feed}(t=\text{End})}}{2} \quad (\text{Eq. 5})$$

where $C_{\text{Feed}(t=0)}$ ($\text{mg} \cdot \text{L}^{-1}$) is the initial concentration and $C_{\text{Feed}(t=\text{End})}$ ($\text{mg} \cdot \text{L}^{-1}$) is the final concentration in the feed solution, respectively.

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3 212 Rejection is usually calculated for one type of solute/molecule. In this study, rejection is also used for
4 213 the BOD₇ parameter, which includes all types of organic solutes that can be biologically degraded,
5 214 irrespective of the individual solute characteristics, such as charge and size. This affects the
6 215 comparison of BOD₇ rejection values across different pre-treatment methods. The pre-treatment
7 216 methods produce FO feed waters with different molecular compositions, meaning that the solutes that
8 217 contribute to the BOD₇ value may be different depending on the pretreatment method. Two feed
9 218 waters can thereby have the same BOD₇ value but a completely different molecular composition,
10 219 which may affect the FO rejection value. Therefore, the BOD₇ rejection values for the FO membranes
11 220 can only be directly compared for water that has undergone the same pre-treatment method.

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16 221 **Results and Discussion**

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18 222 Different FO feed types were produced from each treatment path (see Figure 1): MSF and MSF+MFP.
19 223 The following symbols in Figures 3 to 6 represent the AIM and HTI water flux (J_w , L·m⁻²·h⁻¹): (X) MSF-
20 224 AIM, (Δ) MFP-AIM and (○) MFP-HTI. Furthermore, the initial and final water flux values for calculating
21 225 the water flux decrease ($J_{w,\%}$, %) can be found in the Supplementary Material (Table A).

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24 226 In Figures 3 to 6, the solute rejections (R, %) of BOD₇, TPt and TPs are displayed as bar graphs. The
25 227 corresponding FO permeate concentrations (c_{Permeate} , mg·L⁻¹) are shown as values inside the
26 228 respective bars. Both values, i.e., R and c_{Permeate} , are displayed together because the initial BOD₇
27 229 concentration in the microsieve filtrate is higher than that in the microfiltration permeate, giving
28 230 mathematically lower rejection values for the FO experiments with microfiltration permeate than those
29 231 with the microsieve filtrate at an identical FO permeate concentration.

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33 232 **Raw wastewater characteristics**

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35 233 The wastewater feed to the pilot-scale plant was sampled after the sand trap (Raw), which is shown in
36 234 Figure 1. The samples collected at this point also include internal streams occurring at the Källby
37 235 WWTP, i.e., anaerobically digested centrate and chemically precipitated sludge from the tertiary
38 236 treatment (P removal with FeCl₃). The total number of samples (n), average concentrations (Avg.,
39 237 mg·L⁻¹), minimum (Min) and maximum (Max) concentrations (mg·L⁻¹) and standard deviation (Std.)
40 238 values are shown in Table 2.

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44 239 **Water flux and solute rejections**

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46 240 **Pre-treatment with only coagulation**

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48 241 By adding PACl (AlCl₃) to (waste) water, Al³⁺ and Cl⁻ dissociate, where Al³⁺ precipitates with
49 242 phosphorus to form AlPO₄ and the free chloride tends to bind to the membrane's surface, leading to a
50 243 more negatively charged membrane [39-40]. Naturally occurring cations, e.g., Ca, Fe and Al, in the
51 244 wastewater could be attracted to the negatively charged surface groups of the MFP-AIM and MFP-HTI
52 245 membranes, leading to an overall charge neutralization and flux decrease [32].

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56 246 The MSF-AIM average water flux was 8.9 L·m⁻²·h⁻¹, starting from an initial value of 9.7 L·m⁻²·h⁻¹ and
57 247 decreasing by 10% to a final water flux of 8.7 L·m⁻²·h⁻¹ after 4.5 h (see Figure 3). The final

concentrations and solute rejections in the AIM-MSF permeate were 6.6 mg L^{-1} (98%) for BOD_7 and 0.06 mg L^{-1} (>99%) for both TPt and TPs (see Figure 3 and Table 3).

The MFP-AIM and MFP-HTI average water fluxes were $11.0 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ and $10.2 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$, respectively, exhibiting similar flux patterns, as shown in Figure 3. The decrease in the MFP-AIM water flux was 21%, from $13.2 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ to $10.4 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$, and the MFP-HTI decrease was 15%, from $11.6 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ to $9.9 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$. However, within the first 0.5 h of the experiment, the MFP-AIM water flux dropped to $12.0 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$, resulting in a water flux decrease of 13%, while the change over the remaining time was similar to that of the HTI membrane (15%).

The final concentrations and solute rejections in the MFP-AIM permeate were $3.4 \text{ mg}\cdot\text{L}^{-1}$ (87%) for BOD_7 and $0.05 \text{ mg}\cdot\text{L}^{-1}$ for both TPt and TPs, corresponding to solute rejections of 88% and 61%, respectively. The MFP-HTI permeate exhibited concentrations and solute rejections of $5.6 \text{ mg}\cdot\text{L}^{-1}$ (76%) for BOD_7 , $0.14 \text{ mg}\cdot\text{L}^{-1}$ (66%) for TPt and $0.05 \text{ mg}\cdot\text{L}^{-1}$ (62%) for TPs (see Figure 3 and Table 4) for both MFP-AIM and MFP-HTI.

Furthermore, with the increasing number of mechanical pre-treatment steps, i.e., MS and MF, the MFP-AIM water flux was higher than that of MSF-AIM, which could be attributed to the absence of SS. This observation agrees with the findings in Kim et al. [25] and Go et al. [26] reporting a noticeable flux decline in case of existing SS. In addition, Hancock et al. [27] reported that an increase of total suspended solids (TSS) concentration resulted in incremental flux decline. Moreover, since the initial BOD_7 concentration in the microfiltration permeate was low, simultaneous reduction of dissolved organic carbon (DOC) being a contributing factor to organic fouling on the TFC membranes was assumed [41].

Pre-treatment with coagulation and anionic flocculation

The combination of coagulant and anionic flocculant can increase the SS, BOD_7 and TPt removal upon applying MS [34] and MS+MF [14] in comparison to only PACl, in which the TPs is significantly removed.

The average MSF-AIM water flux was $9.8 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$, where the initial water flux was $12.3 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ and it reached a final flux of $9.3 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ at the end of the experiment, resulting in a water flux decrease of 24%. The final concentrations and solute rejections in the MSF-AIM permeate were found to be $5.4 \text{ mg}\cdot\text{L}^{-1}$ (72%) for BOD_7 and $0.05 \text{ mg}\cdot\text{L}^{-1}$ both TPt and TPs (corresponding to 98% and 82%, respectively); see Figure 4 and Table 5 for more details.

During the coagulation and flocculation, the created flocs increase their binding strengths by the addition of an anionic polymer linking the negatively charged polymer groups to the positively charged sites in the flocs. The created flocs (SS) can be removed with MS and MS+MF (see Table 5 and 6). The remaining SS in the microsieve filtrate is assumed to be less prone to interact with the MSF-AIM membrane surface, which could explain the higher MSF-AIM water flux in comparison with only PACl.

The initial water fluxes for the MFP-AIM and MFP-HTI membranes were $13.0 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ and $14.8 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$, respectively. The final water flux was $10.8 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ for the MFP-AIM membrane and $12.5 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$

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¹ for the MFP-HTI membrane, resulting in water flux decreases of 17% and 16%, respectively (see Figure 4).

Microfiltration removes SS and thereby reduces the amount of foulants, e.g., BOD₇, assuming the simultaneous reduction of DOC in the feed solution, which is consistent with higher MFP-AIM and MFP-HTI water fluxes. The final concentrations in the MFP-AIM and MFP-HTI permeates were almost identical with respect to BOD₇ (5.0 mg·L⁻¹ for MFP-AIM and 4.7 mg·L⁻¹ for MFP-HTI), corresponding to 86% and 87% solute rejections, respectively. The TPt and TPs concentrations were 0.04 mg·L⁻¹ in both the MFP-AIM (86% for TPt of and 37% for TPs of) and MFP-HTI permeates (87% and <1%), as shown in Table 6 and Figure 4. The low TPt and TPs rejections (see Figure 4) were due to the low initial TPt and TPs concentrations (0.04 mg·L⁻¹) in the microfiltration permeate (see Table 6).

Coagulation and cationic flocculation

PACl with cationic flocculant was applied by Remy et al. [36] to remove carbon and phosphorous with MS, similar to the studies of Väänänen et al. [34] and Hey et al. [14]. The concentrations shown in Table 7 and 8 are in line with these studies.

The MSF-AIM initial water flux was 10.6 L·m⁻²·h⁻¹, and it declined by 19% to a final value of 8.6 L·m⁻²·h⁻¹ at the end of the experiment (see Figure 5). The final concentration and solute rejection in the MSF-AIM permeate was 18.2 mg·L⁻¹ (44%) for BOD₇ and 0.05 mg·L⁻¹ (78% and 8%) for both TPt and TPs, as presented in Table 7 and Figure 5.

After MF, the BOD₇ concentration (16 mg·L⁻¹) in the microfiltration permeate remained stable, whereas the TPt and TPs were reduced further to <0.03 and 0.04 mg·L⁻¹ by precipitation with PACl (see Table 8); thus, that the rejections for both TPt and TPs were <1% (see Figure 5).

The initial water flux for the MFP-AIM membrane was 10.4 L·m⁻²·h⁻¹, and it decreased by 13% to a final value of 9.1 L·m⁻²·h⁻¹. The MFP-HTI water flux decreased by 15% from an initial value of 11.7 L·m⁻²·h⁻¹ to 9.9 L·m⁻²·h⁻¹. However, within the first 15 minutes of the MFP-HTI experiment, the water flux dropped to 10.4 L·m⁻²·h⁻¹ before decreasing steadily by 5% until achieving a final water flux of 9.9 L·m⁻²·h⁻¹, as shown in Figure 5. The FO permeate quality showed that the BOD₇ concentration was 3 times higher following the MFP-AIM membrane (14.5 mg·L⁻¹) in comparison to the MFP-HTI membrane (4.8 mg·L⁻¹). The TPt and TPs concentrations were below the quantification limit in both the MFP-AIM and MFP-HTI permeates (see Table 8). Previously, the AIM membrane has been shown to exhibit a higher rejection of small uncharged organic molecules compared to the HTI membrane [3,19]. Therefore, based on previous findings, the AIM membrane is expected to perform better than the HTI membrane if the rejection is due to size exclusion. Thus, it may seem surprising in this study that the HTI membrane exhibited the highest rejection. The better rejection of the HTI membrane in this case could be due to other effects, such as differences in the membrane charge leading to a difference in the rejection of charged molecules or a difference in the adsorption capability. If a larger amount of BOD can be adsorbed onto the HTI membrane, this could lead to a higher initial apparent rejection until saturation is reached. Finally, it is also possible that this single HTI result is an outlier because it is the only experiment in which the two membranes were found to deviate significantly.

Cationic flocculation

The addition of only cationic flocculant, which is also described as cationic polymer coagulation by Kvinnesland and Ødegaard [42], leads to the binding of the negatively charged SS, creating macro-flocs. However, the cationic polymer does not precipitate soluble phosphorus (TPs), which is shown in Tables 9 and 10.

The MSF-AIM initial water flux was $10.2 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ and reached a final flux of $8.8 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ at the end of the experiment, corresponding to a decrease in the water flux of approximately 14%, as shown in Figure 6. The final concentrations in the MSF-AIM permeate were $20.8 \text{ mg}\cdot\text{L}^{-1}$ for BOD_7 and $0.1 \text{ mg}\cdot\text{L}^{-1}$ for TPt and TPs (see Table 9).

The MFP-AIM water flux declined by 35% from $13.7 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ to $8.9 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$, whereas the MFP-HTI declined by 2% from $13.2 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ to $12.9 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ (see Figure 6). The steep decline for the MFP-AIM membrane has been previously observed in a similar experiment with an identical setup (data not shown); therefore, membrane or system failure was disregarded. The duration of the MFP-HTI water flux assessment was 3.5 h instead of 4.5 h, which was caused by an abrupt stop in the electronic weight measurement and recording (see the vertical dotted line in Figure 6). Therefore, the average water fluxes of the MSF-AIM and MFP-AIM were adjusted to $9.0 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$, $10.6 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ and $12.7 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ for MSF-AIM, MFP-AIM, and MFP-HTI, respectively, for comparison.

The BOD_7 concentrations in the MFP-AIM and MFP-HTI permeates were $14.4 \text{ mg}\cdot\text{L}^{-1}$ and $15.1 \text{ mg}\cdot\text{L}^{-1}$, respectively. In comparison to the AIM results with coagulation and cationic flocculation, the AIM permeate quality was similar, indicating that coagulation does not affect the BOD_7 removal of the AIM membrane. For the HTI membrane, however, the permeate quality is now comparable to the AIM membrane, indicating that either the coagulation positively affects the HTI membrane and not the AIM membrane or that one of the results might be an outlier. Furthermore, the TPt and TPs concentrations found in both permeates were $0.05 \text{ mg}\cdot\text{L}^{-1}$ for the MFP-AIM and MFP-HTI membranes (see Table 10).

The addition of only cationic polymer was found to have less of an effect on the MSF-AIM water flux in comparison to MFP-AIM. This might be consistent with the formation of a protective layer by organic foulants, e.g., SS, which are caused by bacterial deposits on the MSF-AIM membrane surface [16]. Hence, the MSF-AIM membrane surface is less exposed to the possible remains of the cationic polymer and other cationic species (e.g., Ca, Fe, and Al) in comparison to the MFP-AIM membrane using a particle-free feed. This could explain the behaviours of the observed MSF-AIM water fluxes in the aforementioned experiments except for PACl with anionic polymer. Furthermore, because TFC membranes are often negatively charged, it is assumed that the AIM surface is more negatively charged than the HTI membrane (-32 mV at pH 7), thus having a higher fouling potential of cationic species [43-44].

Summary and discussion of the results

Aquaporin Inside™ with microsieve filtrate

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Comparing all of the MSF-AIM results in Figure 7, only the PACl + anionic polymer pre-treatment experiment resulted in a higher water flux compared to the mechanical pre-treatment [16]. The pre-treatments with coagulation and/or flocculation resulted in slightly lower water flux values. In general, the water flux differences were very small and most likely within what can be expected from random fluctuations in the membrane performance and water quality. This means that regardless of the applied pre-treatment method, including microsieving, the fouling potential is unaffected (see Figure 7). The reason for this may be that the foulants are not sufficiently chemically affected by coagulation and/or flocculation to be completely removed by the microsieve. Thus, the foulants continue through the microsieve and can affect the membrane. Although the fouling potential is not significantly altered, a stable water flux was obtained with only a slight decline during several hours of operation. This is important for the rate at which membrane cleaning, e.g., CIP, will be necessary.

It is speculated that the created flocs passing through the microsieve can act as a protective (cake) layer, reducing the potential to interact with the membrane surface [44]. Regardless of the applied physicochemical pre-treatment method, the MSF-AIM permeate quality, i.e., BOD₇, did not improve in comparison to the mechanical pre-treatment, as shown in Table 11. However, the MSF-AIM permeates with only PACl and with PACl + anionic polymer satisfied the Swedish wastewater discharge demands for small and medium-sized WWTPs.

Aquaporin Inside™ with microfiltration permeate

The highest water fluxes were obtained for MFP-AIM (12.0 L·m⁻²·h⁻¹) and MSF-AIM (9.8 L·m⁻²·h⁻¹) when applying PACl+anionic polymer. The obtained MFP-AIM water flux was improved by 10% and by 20% upon applying only PACl (11.0 L·m⁻²·h⁻¹) and PACl + anionic polymer (12.0 L·m⁻²·h⁻¹), respectively, in comparison to the mechanical pre-treatment (10.0 L·m⁻²·h⁻¹), which is shown in Figure 8. Furthermore, the MFP-AIM water flux with only cationic polymer obtained a 9% higher flux, although it declined linearly by 35%, reaching a zero water flux within 13 hours if extrapolated. The MFP-AIM permeate qualities were 3.4 mg·L⁻¹ (PACl only) and 5.0 mg·L⁻¹ (PACl + anionic polymer), and they were ≤ 0.06 mg·L⁻¹ for TPT and TPs. In comparison to the mechanical pre-treatment, the MFP-AIM water flux was improved, although the BOD₇ concentrations in the permeates were 8 and 12 times higher. In addition, the BOD₇ concentrations in the permeates for the PACl + cationic polymer and cationic polymer were significantly higher, i.e., 16.8 mg·L⁻¹ and 14.4 mg·L⁻¹, respectively, in comparison to the concentrations with PACl only and PACl + anionic polymer. In conclusion, the MFP-AIM permeate with only PACl and PACl + anionic polymer were found to satisfy the Swedish wastewater discharge demand for small and medium-sized WWTPs.

HTI with microfiltration permeate

Physicochemical pre-treatment using PACl + anionic polymer on the MFP-HTI membrane improved the water flux by 19% (13.4 L·m⁻²·h⁻¹) in comparison to the water flux with mechanical pre-treatment (10.8 L·m⁻²·h⁻¹), which is shown in Figure 9. However, the BOD₇ concentration in the MFP-HTI permeate with PACl + anionic polymer (4.7 mg·L⁻¹) was 3.5 times higher than in the MFP-HTI permeate with mechanical pre-treatment (1.5 mg·L⁻¹), which is shown in Table 11. Furthermore, the

use of cationic polymer on the MFP-HTI membrane increased the water flux by 15% to $12.7 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ and showed a water flux decrease of only 2% in comparison to the water flux with only mechanical pre-treatment, i.e., $10.8 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$, corresponding to a decrease of 36%. However, the BOD_7 concentrations with cationic polymer in the MFP-HTI permeate were 10 times higher in comparison to those with the mechanical pre-treatment and 3 times higher than those with PACI + anionic polymer. The permeate quality with PACI + cationic polymer was similar to the result with PACI + anionic polymer ($4.7 \text{ mg}\cdot\text{L}^{-1}$), which can be questioned because the BOD_7 concentration in all permeates (including AIM) involving the cationic polymer were at least 3 times higher than that with only PACI or PACI + anionic polymer.

Conclusions

The physicochemical pre-treatment of municipal wastewater in combination with forward osmosis can be applied with TFC AIM and HTI membranes for municipal wastewater treatment. This study showed that the addition of coagulant and/or flocculant can affect the water flux, water flux decrease and permeate concentration, i.e., BOD_7 , TPt and TPs. PACI and anionically charged and polyacrylamide-based flocculant in combination with microsieving and microfiltration achieved the highest water flux for both the MFP-AIM ($12.0 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$) and MFP-HTI ($13.4 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$) membranes compared to only mechanical pre-treatment ($10.0 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ and $10.8 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$, respectively). In addition, the same treatment configuration (PACI + anionic polymer) achieved the highest water flux with MSF as feed on the AIM membrane ($9.8 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$). The MFP-AIM and MFP-HTI permeates satisfied the Swedish discharge demands for small and medium-sized wastewater treatment plants regarding the BOD_7 , TPt and TPs concentrations in the permeate. The addition of only coagulant resulted in the lowest BOD_7 , TPt and TPs concentrations in the permeate. However, all tested physicochemical pre-treatment configurations exhibited at least double the BOD_7 concentration (range: 3.4 to $20.8 \text{ mg}\cdot\text{L}^{-1}$) in both the AIM and HTI permeates compared to only mechanical pre-treatment (range: 0.3 - $1.5 \text{ mg}\cdot\text{L}^{-1}$).

The addition of a physicochemical pre-treatment stage before FO requires higher capital costs but requires 20% less FO membrane area compared to mechanical pre-treatment. The operational and economic advantages and disadvantages need to be investigated.

Based on the findings of this study, in comparison with only mechanical pre-treatment, the physicochemical pre-treatment of municipal wastewater prior to FO can increase the water flux by up to 20%, although it does not improve the permeate quality of the investigated compounds, i.e., BOD_7 , TPt and TPs, because both the AIM and HTI membranes seem to perform well alone.

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The effects of physicochemical wastewater treatment operations on forward osmosis
effects of physicochemical pre-treatment of municipal wastewater on forward osmosis

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Abstract

Raw municipal wastewater from a full-scale wastewater treatment plant was physicochemically pre-treated in a large pilot-scale system comprising coagulation, flocculation, microsieving and microfiltration operated in various configurations. The produced microsieving filtrates and microfiltration permeates were then concentrated using forward osmosis (FO). Aquaporin Inside™ FO membranes were used for both the microsieving filtrate and microfiltration permeates, and HTI-TFC membranes for the microfiltration permeate using only NaCl as the draw solution. The FO performance was evaluated in terms of the water flux, water flux decline and solute rejections of biochemical oxygen demand and total and soluble phosphorus. The obtained results were compared with the results of forward osmosis after only mechanical pre-treatment. The FO permeates satisfied the Swedish discharge demands for small and medium-sized wastewater treatment plants. The study demonstrates that physicochemical pre-treatment can improve the FO water flux by up to 20%. In contrast, the solute rejection decreases significantly compared to the FO-treated wastewater with mechanical pre-treatment.

Key words: Forward osmosis, non-biological treatment, microfiltration, microsieving, physicochemical pre-treatment, wastewater treatment

33 **Introduction**

34 The need to recover valuable resources from wastewater has been emphasized over the past 20
35 years, in which the direct utilization of nutrients from municipal wastewater has been described as
36 (direct) sewer mining [1-3]. Membrane technologies such as microfiltration (MF) and ultrafiltration (UF)
37 have proven to be successful separation techniques to produce on-demand nutrient-rich water that is
38 free of particles and pathogens and hence suitable for irrigation [4].

39 The concept of municipal wastewater treatment using membrane filtration without biological treatment
40 steps has been referred to as direct membrane filtration, direct membrane separation and direct
41 sewage microfiltration [5-7]. The direct membrane filtration (DMF) concept has been tested on different
42 wastewater types, such as raw municipal wastewater, primary settler effluent, domestic wastewater
43 from an apartment and a dormitory complex and grey water [5-13]. However, as the DMF concept only
44 retains particles and bacteria, the reported permeate quality did not satisfy the present Swedish
45 wastewater discharge demands for small and medium-sized wastewater treatment plants (WWTPs)
46 because the soluble carbon and phosphorus (and nitrogen) are not retained. By combining DMF with
47 physicochemical pre-treatments, such as coagulation and flocculation, it is possible to meet the
48 wastewater discharge demands, as shown in the pilot-scale study by Hey et al. [14], requiring
49 0.4 kWh·m⁻³ treated wastewater. However, if higher levels of removal are required, more advanced
50 techniques must be added to the wastewater treatment process. The same study also showed a
51 significant improvement in the MF permeate flux by 20% in comparison to mechanical pre-treatment
52 only, i.e., microsieve (MS) and MF.

53 In addition to the non-biological DMF concept, the forward osmosis (FO) membrane process has been
54 suggested as a promising technology with the ability to concentrate wastewater [2,3,15] with high
55 retentions of biochemical oxygen demand [16], chemical oxygen demand [15] and total and soluble
56 phosphorus [15,16]. In comparison to a pressure-driven membrane process, e.g., MF, the FO process
57 operates at a non-hydraulic pressure, utilizing the osmotic pressure difference across a semi-
58 permeable FO membrane placed between a feed solution of low osmotic pressure and a draw solution
59 of high osmotic pressure [15]. Because the FO process naturally attempts to achieve an osmotic
60 equilibrium, water moves from the feed solution to the draw solution across the FO membrane,
61 reducing the draw solution's osmotic potential [17]. The reported advantages of FO over pressure-
62 driven membrane processes include its lower fouling propensity [18], high water flux recovery [17],
63 high rejection of a wide range of trace organic compounds [19-21] and heavy metals [22] and reduced
64 capital and operational costs [18]. FO membrane studies have been performed with different
65 wastewater types, such as municipal wastewater and synthetic wastewater [15,16,18,22-2427].

66 Few studies have reported the effects of using different pre-treatment methods, e.g., mechanical [16]
67 and physicochemical, before FO. In fact, the FO process is mostly considered as a pre-treatment step
68 to concentrate wastewater [2528]. Coday et al. [21] suggested coagulation, flocculation or MF as
69 suitable pre-treatment methods before FO, while Lutchmiah et al. [2629] argued that extensive pre-
70 treatment systems for FO may be redundant when treating complex feeds, depending on the FO
71 membrane performance. However, the amount of publications considering physicochemical pre-

~~treatment of municipal wastewater before FO is limited. However, no studies have been published on the physicochemical pre-treatment of municipal wastewater before FO.~~

In contrast, several studies have been conducted by treating water or wastewater with coagulation and/or flocculation as a pre-treatment to pressure-driven membrane (MF or UF) processes to prevent fouling [27,2830-31]. Coagulation has been found to be the most successful pre-treatment for fouling reduction on thin film composite (RO-TFC) membranes, reducing the dissolved organic carbon (DOC), which is an important fouling factor, by 30%. Furthermore, coagulated flocs can deposit on the membrane surface and act as protection for the membrane, whereas the cake layer can easily be removed. However, a proper dosage of coagulant and flocculant prevents membrane fouling and can enhance membrane performance, whereas overdosing by a small amount, e.g., 50 ppb of Al^{3+} , can foul the membrane [2932]. Furthermore, insoluble coagulants can form preflocs that attach to any surface and neutralize its charge. For flocculation, polyacrylamide polymer can cause membrane damage by covering the polyamide surface, which can be prevented by accounting for the molecular weight, charge density, solubility and charge position. Furthermore, anionic charged polymers have been shown to be better at removing organic and cationic compounds compared to cationic charged polymers, enhancing the MF water flux [14,2932].

The scope of this study is to ascertain the effects of the physicochemical pre-treatment of municipal wastewater before FO, including coagulation, flocculation (anionic- or cationic-charged polyacrylamide-based polymer), microsieving and microfiltration. The produced feed types from a pilot-scale setup were tested on two different thin-film composite (TFC) FO membranes, and the performance was characterized in terms of the water flux, water flux decrease and solute rejection. ~~The membranes were not compared with respect to reverse salt flux and concentration polarization effects.~~ Furthermore, the achieved results were evaluated and compared with the FO results from wastewater with only mechanical pre-treatment [16]. The final concentrations of the biochemical oxygen demand (BOD_7) and the total and soluble phosphorus (TPt and TPs) in the FO permeate were evaluated to meet the Swedish discharge demands for small and medium-sized WWTPs (BOD_7 15 $\text{mg}\cdot\text{L}^{-1}$ and TPt 0.5 $\text{mg}\cdot\text{L}^{-1}$).

Materials and Methods

At the Källby WWTP, Lund, Sweden, the incoming wastewater is of medium strength (see Table 2) according to the criteria described by Tchobanoglous et al. [3033]. The wastewater is treated with 6-mm perforated hole-plate bar screens (EscaMax, Huber AG, Germany) with subsequent sand removal in a sand trap. The internal streams occurring at the WWTP, i.e., centrate water from the anaerobic digester and chemically precipitated sludge from the tertiary treatment step (P removal with FeCl_3), are released before the sand trap (see Figure 1). Because the screen and the sand trap are part of the mechanical treatment steps in WWTPs [3033], the term pre-treatment in this study is defined as the treatment methods applied between the sand trap outlet and forward osmosis. Aquaporin Inside™ (Aquaporin A/S, Denmark) and Hydration Technologies Inc. (Albany, OR, USA) FO membranes are henceforth referred to as AIM and HTI, respectively.

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To test the effect of the different physicochemical pre-treatment configurations before FO (see Figure 1 and Table 1), a pilot-scale plant was constructed. The feed to the pilot-scale plant was taken at the sand trap outlet (Raw), where the coagulation and flocculation were followed by mechanical pre-treatment steps that included MS followed by MF. Each treatment configuration, as presented in Table 1, was operated for more than 6 days to ensure stable MF operation before a grab sample was obtained to be subjected to forward osmosis [14]. Furthermore, each grab sample, e.g., microsieve filtrate (MSF) and microfiltration permeate (MFP), was collected at different points.

A schematic of the pilot-scale plant is shown in Figure 1. The upper treatment path is described as MS, including only the microsieve, and the MSF is used as a feed solution for the AIM (MSF-AIM). The lower treatment path, described as MS+MF, includes MS and MF, where the produced MF permeate (MFP) is used as the feed solution for both the AIM (MFP-AIM) and HTI (MFP-HTI) FO membranes. The black dots in Figure 1 represent the sampling points at the sand trap outlet (Raw), MSF and MFP.

Coagulation and flocculation

Coagulation and flocculation were performed with the coagulant and/or flocculant added proportionally ($\text{L}\cdot\text{m}^{-3}$) to the feed before entering the respective mixing tanks. In the coagulation step, polyaluminum chloride (PACl; Kemira, Sweden) was used to reach a final concentration of $15\text{ mg}\cdot\text{L}^{-1}$ in the feed and mixed with a velocity gradient (G-value) of $100\text{--}200\text{ s}^{-1}$. For flocculation, either anionically or cationically charged polyacrylamide-based polymers (Veolia, France) were used. The flocculant was dosed in the same manner as the coagulant to a final feed concentration of $3\text{ mg}\cdot\text{L}^{-1}$ (anionic polymer) or $4\text{ mg}\cdot\text{L}^{-1}$ (cationic polymer) with a G-value of $80\text{--}150\text{ s}^{-1}$. The coagulation and flocculation structure was identical to that described in Väänänen et al. [3434].

Microsieve

A drum rotating microsieve (HDF801-1H, Hydrotech AB, Sweden) with a total filter area of 0.33 m^2 and pore openings of $100\text{ }\mu\text{m}$ was operated at $2.0\text{ m}^3\cdot\text{h}^{-1}$. The produced microsieve filtrate was either used directly as the feed solution for FO (MS treatment path) or as the feed for microfiltration (MS+MF treatment path), as shown in Figure 1. The operational principle of the microsieve filter is described in Ljunggren et al. [3235], and the operation, including the filter cloth cleaning, is described in Remy et al. [3336] and Väänänen et al. [3434].

Microfiltration

MF was performed with five flat-sheet membranes (MFP2, Alfa Laval A/S, Denmark) assembled in a plate and frame module, resulting in a 1.025 m^2 effective membrane area with a nominal pore size of $0.2\text{ }\mu\text{m}$. The microsieve filtrate was always used as the feed for the MF, as shown in Figure 1. The MF was operated in outside-in mode at a constant hydrostatic pressure of 3 kPa (0.03 bar), which was induced by the feed level over the membrane. Permeate was produced in 10-min cycles, each followed by 2 min of membrane relaxation with no back-flushing during operation, similar to the method described by Abdessemed et al. [9]. Scouring air was continuously supplied from the bottom of the membrane module with a specific air demand of $0.69\text{ Nm}^3\cdot\text{m}^{-2}\cdot\text{h}^{-1}$, which was controlled by an

air flow meter. The hydraulic retention time in the MF tank was less than 6 min to avoid biological activity in the tank. A more detailed description of the pilot-scale plant setup and the conducted experiments can be found in Hey et al. [14].

Forward osmosis

Forward osmosis membranes

FO experiments were conducted with two types of flat-sheet TFC FO membranes: AIM (from Aquaporin A/S, Denmark) and HTI (from Hydration Technology Innovations, Albany, OR, USA). The AIM membrane is a modified TFC membrane with an active layer (AL) containing biomimetic aquaporin proteins reconstituted in spherical vesicles encapsulated by a polyamide thin film supported by polyethersulphone (PES) [3437]. The HTI TFC membrane is prepared using polyamide embedded on a polysulfone support [3538].

Experimental overview

The microfiltration permeate feed types were tested with AIM and HTI membranes, whereas the microsieve filtrate feed was only tested with the AIM membrane because the HTI membranes were no longer available from the supplier. Table 1 shows the different pilot-scale pre-treatment configurations, producing FO feed that then was used in the AIM and HTI membrane experiments.

Liquid sampling and analysis

Depending on the experiment, MS (upper treatment path in Figure 1) or MS+MF (lower treatment path in Figure 1) grab samples were collected at the sampling points (Raw, MSF and MFP) shown as black dots in Figure 1. The samples were also obtained from the feed solution and draw solution before and after each FO experiment. Standard methods were used for analysing the suspended solids (SS, ISO 11923:1997), BOD₇ (ISO 5815-1;2:2003), TPt and TPs (ISO 6878:2004).

Forward osmosis experimental configuration

Two identical configurations were installed to conduct experiments in parallel with the AIM and HTI membranes. Each configuration comprised a rectangular membrane module with a membrane separating two identical compartments, each with dimensions of 175 mm (length), 80 mm (width) and 1.3 mm (height). The active tested membrane area was 140 cm². Both the AIM and HTI membranes were tested with the active layer (AL) facing the feed solution (FS), denoted as AL-FS mode. A mesh spacer with a thickness of 1 mm was placed on the support side of the membrane. A flow rate of 260 mL·min⁻¹ was used, generating a cross-flow velocity (u_{cr}) of 4.17 cm·s⁻¹, and the counter-current circulation of the feed and draw solutions was created by two micro-gear pumps (WT3000-1JB/M, Longer Pump, China) connected with Tygon®-tubing (R-3603, Saint-Gobain Performance Plastics France – Site de Charny, France).

The draw solution (2 M NaCl) and feed solution were kept in 5-L reservoirs with a volume of 2 L at the beginning of each FO experiment. During the experiment, the mass change of the draw solution was measured with an electronic balance (FKB36K0.1, Kern & Sohn GmbH, Germany) sampled every 5

minutes. All experiments were conducted at room temperature, $20^{\circ}\text{C} \pm 2^{\circ}\text{C}$. A schematic of the laboratory FO setup is shown in Figure 2. The duration of each experiment was 4.5 h.

Quantification of water flux, water flux decrease, solute concentration and rejection

The average water flux (J_W , $\text{L} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$) was determined using an electronic balance, monitoring the rate at which the weight of the draw solution increased:

$$J_W = \frac{V_{\text{Permeate}}}{A_m \cdot \Delta t} \quad (\text{Eq. 1})$$

where V_{Permeate} (L) is the permeate volume during the experiment, which is defined as the difference between the final volume of the draw solution ($V_{\text{Draw}(t = \text{End})}$, L) and the initial volume of the draw solution ($V_{\text{Draw}(t = 0)}$, L). A_m (m^2) is the effective FO membrane surface area (0.014 m^2), and Δt (h) is the experimental time duration.

The water flux decrease ($J_{W,\%}$, %) was calculated without accounting for the dilution of the draw solution:

$$J_{W,\%} = \frac{J_W(t=0) - J_W(t=\text{End})}{J_W(t=0)} \quad (\text{Eq. 2})$$

where $J_{W(t=0)}$ ($\text{L} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$) is the initial water flux, and $J_{W(t=\text{End})}$ ($\text{L} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$) is the final water flux.

To evaluate the quality of the produced FO permeate, the final concentrations (c_{Permeate} , $\text{mg} \cdot \text{L}^{-1}$) of BOD_7 , TPT and TPs were calculated,

$$c_{\text{Permeate}} = \frac{V_{\text{Draw}(t=\text{End})} \cdot c_{\text{Draw}(t=\text{End})} - V_{\text{Draw}(t=0)} \cdot c_{\text{Draw}(t=0)}}{V_{\text{Permeate}}} \quad (\text{Eq. 3})$$

where $V_{\text{Draw}(t=\text{End})}$ (L) is the final volume and $c_{\text{Draw}(t=\text{End})}$ ($\text{mg} \cdot \text{L}^{-1}$) is the final concentration in the draw solution, $V_{\text{Draw}(t=0)}$ (L) is the initial volume and $c_{\text{Draw}(t=0)}$ ($\text{mg} \cdot \text{L}^{-1}$) is the initial concentration in the draw solution, and V_{Permeate} (L) is the permeate volume during the experiment, which is defined as the difference between the final volume of the draw solution ($V_{\text{Draw}(t=\text{End})}$, L) and the initial volume of the draw solution ($V_{\text{Draw}(t=0)}$, L).

The solute rejection (R, %) was calculated as follows:

$$R (\%) = 1 - \frac{c_{\text{Permeate}}}{c_{\text{Feed(Avg)}}} \cdot 100\% \quad (\text{Eq. 4})$$

where R (%) is the solute rejection, c_{Permeate} ($\text{mg} \cdot \text{L}^{-1}$) is the concentration in the permeate, and $c_{\text{Feed(Avg.)}}$ ($\text{mg} \cdot \text{L}^{-1}$) is the average concentration in the FS during the experiment; see Liu et al. [20] for further details.

The average concentration in the feed solution was calculated as follows:

$$c_{\text{Feed(Avg.)}} = \frac{c_{\text{Feed}(t=0)} + c_{\text{Feed}(t=\text{End})}}{2} \quad (\text{Eq. 5})$$

where $c_{\text{Feed}(t=0)}$ ($\text{mg} \cdot \text{L}^{-1}$) is the initial concentration and $c_{\text{Feed}(t=\text{End})}$ ($\text{mg} \cdot \text{L}^{-1}$) is the final concentration in the feed solution, respectively.

Rejection is usually calculated for one type of solute/molecule. In this study, rejection is also used for the BOD₇ parameter, which includes all types of organic solutes that can be biologically degraded, irrespective of the individual solute characteristics, such as charge and size. This affects the comparison of BOD₇ rejection values across different pre-treatment methods. The pre-treatment methods produce FO feed waters with different molecular compositions, meaning that the solutes that contribute to the BOD₇ value may be different depending on the pretreatment method. Two feed waters can thereby have the same BOD₇ value but a completely different molecular composition, which may affect the FO rejection value. Therefore, the BOD₇ rejection values for the FO membranes can only be directly compared for water that has undergone the same pre-treatment method.

Results and Discussion

Different FO feed types were produced from each treatment path (see Figure 1): MSF and MSF+MFP. The following symbols in Figures 3 to 6 represent the AIM and HTI water flux (J_w , L·m⁻²·h⁻¹): (X) MSF-AIM, (Δ) MFP-AIM and (○) MFP-HTI. Furthermore, the initial and final water flux values for calculating the water flux decrease ($J_{w,\%}$, %) can be found in the Supplementary Material (Table A).

In Figures 3 to 6, the solute rejections (R , %) of BOD₇, TPt and TPs are displayed as bar graphs. The corresponding FO permeate concentrations (c_{Permeate} , mg·L⁻¹) are shown as values inside the respective bars. Both values, i.e., R and c_{Permeate} , are displayed together because the initial BOD₇ concentration in the microsieve filtrate is higher than that in the microfiltration permeate, giving mathematically lower rejection values for the FO experiments with microfiltration permeate than those with the microsieve filtrate at an identical FO permeate concentration.

Raw wastewater characteristics

The wastewater feed to the pilot-scale plant was sampled after the sand trap (Raw), which is shown in Figure 1. The samples collected at this point also include internal streams occurring at the Källby WWTP, i.e., anaerobically digested centrate and chemically precipitated sludge from the tertiary treatment (P removal with FeCl₃). The total number of samples (n), average concentrations (Avg., mg·L⁻¹), minimum (Min) and maximum (Max) concentrations (mg·L⁻¹) and standard deviation (Std.) values are shown in Table 2.

Water flux and solute rejections

Pre-treatment with only coagulation

By adding PACl (AlCl₃) to (waste) water, Al³⁺ and Cl⁻ dissociate, where Al³⁺ precipitates with phosphorus to form AlPO₄ and the free chloride tends to bind to the membrane's surface, leading to a more negatively charged membrane [36,3739-40]. Naturally occurring cations, e.g., Ca, Fe and Al, in the wastewater could be attracted to the negatively charged surface groups of the MFP-AIM and MFP-HTI membranes, leading to an overall charge neutralization and flux decrease [2932].

The MSF-AIM average water flux was 8.9 L·m⁻²·h⁻¹, starting from an initial value of 9.7 L·m⁻²·h⁻¹ and decreasing by 10% to a final water flux of 8.7 L·m⁻²·h⁻¹ after 4.5 h (see Figure 3). The final

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concentrations and solute rejections in the AIM-MSF permeate were 6.6 mg L⁻¹ (98%) for BOD₇ and 0.06 mg L⁻¹ (>99%) for both TPt and TPs (see Figure 3 and Table 3).

The MFP-AIM and MFP-HTI average water fluxes were 11.0 L·m⁻²·h⁻¹ and 10.2 L·m⁻²·h⁻¹, respectively, exhibiting similar flux patterns, as shown in Figure 3. The decrease in the MFP-AIM water flux was 21%, from 13.2 L·m⁻²·h⁻¹ to 10.4 L·m⁻²·h⁻¹, and the MFP-HTI decrease was 15%, from 11.6 L·m⁻²·h⁻¹ to 9.9 L·m⁻²·h⁻¹. However, within the first 0.5 h of the experiment, the MFP-AIM water flux dropped to 12.0 L·m⁻²·h⁻¹, resulting in a water flux decrease of 13%, while the change over the remaining time was similar to that of the HTI membrane (15%).

The final concentrations and solute rejections in the MFP-AIM permeate were 3.4 mg·L⁻¹ (87%) for BOD₇ and 0.05 mg·L⁻¹ for both TPt and TPs, corresponding to solute rejections of 88% and 61%, respectively. The MFP-HTI permeate exhibited concentrations and solute rejections of 5.6 mg·L⁻¹ (76%) for BOD₇, 0.14 mg·L⁻¹ (66%) for TPt and 0.05 mg·L⁻¹ (62%) for TPs (see Figure 3 and Table 4) for both MFP-AIM and MFP-HTI.

Furthermore, with the increasing number of mechanical pre-treatment steps, i.e., MS and MF, the MFP-AIM water flux was higher than that of MSF-AIM, which could be attributed to the absence of SS. This observation agrees with the findings in Kim et al. [25] and Go et al. [26] reporting a noticeable flux decline in case of existing SS. In addition, Hancock et al. [27] reported that an increase of total suspended solids (TSS) concentration resulted in incremental flux decline. Moreover, and since the lower initial BOD₇ concentration in the microfiltration permeate was low, assuming the simultaneous reduction of dissolved organic carbon (DOC) being a contributing factor to organic fouling on the TFC membranes was assumed [3841].

Pre-treatment with coagulation and anionic flocculation

The combination of coagulant and anionic flocculant can increase the SS, BOD₇ and TPt removal upon applying MS [3434] and MS+MF [14] in comparison to only PACl, in which the TPs is significantly removed.

The average MSF-AIM water flux was 9.8 L·m⁻²·h⁻¹, where the initial water flux was 12.3 L·m⁻²·h⁻¹ and it reached a final flux of 9.3 L·m⁻²·h⁻¹ at the end of the experiment, resulting in a water flux decrease of 24%. The final concentrations and solute rejections in the MSF-AIM permeate were found to be 5.4 mg·L⁻¹ (72%) for BOD₇ and 0.05 mg·L⁻¹ both TPt and TPs (corresponding to 98% and 82%, respectively); see Figure 4 and Table 5 for more details.

During the coagulation and flocculation, the created flocs increase their binding strengths by the addition of an anionic polymer linking the negatively charged polymer groups to the positively charged sites in the flocs. The created flocs (SS) can be removed with MS and MS+MF (see Table 5 and 6). The remaining SS in the microsieve filtrate is assumed to be less prone to interact with the MSF-AIM membrane surface, which could explain the higher MSF-AIM water flux in comparison with only PACl.

The initial water fluxes for the MFP-AIM and MFP-HTI membranes were 13.0 L·m⁻²·h⁻¹ and 14.8 L·m⁻²·h⁻¹, respectively. The final water flux was 10.8 L·m⁻²·h⁻¹ for the MFP-AIM membrane and 12.5 L·m⁻²·h⁻¹

¹ for the MFP-HTI membrane, resulting in water flux decreases of 17% and 16%, respectively (see Figure 4).

Microfiltration removes SS and thereby reduces the amount of foulants, e.g., BOD₇, assuming the simultaneous reduction of DOC in the feed solution, which is consistent with higher MFP-AIM and MFP-HTI water fluxes. The final concentrations in the MFP-AIM and MFP-HTI permeates were almost identical with respect to BOD₇ (5.0 mg·L⁻¹ for MFP-AIM and 4.7 mg·L⁻¹ for MFP-HTI), corresponding to 86% and 87% solute rejections, respectively. The TPt and TPs concentrations were 0.04 mg·L⁻¹ in both the MFP-AIM (86% for TPt of and 37% for TPs of) and MFP-HTI permeates (87% and <1%), as shown in Table 6 and Figure 4. The low TPt and TPs rejections (see Figure 4) were due to the low initial TPt and TPs concentrations (0.04 mg·L⁻¹) in the microfiltration permeate (see Table 6).

Coagulation and cationic flocculation

PACI with cationic flocculant was applied by Remy et al. [3336] to remove carbon and phosphorous with MS, similar to the studies of Väänänen et al. [3434] and Hey et al. [14]. The concentrations shown in Table 7 and 8 are in line with these studies.

The MSF-AIM initial water flux was 10.6 L·m⁻²·h⁻¹, and it declined by 19% to a final value of 8.6 L·m⁻²·h⁻¹ at the end of the experiment (see Figure 5). The final concentration and solute rejection in the MSF-AIM permeate was 18.2 mg·L⁻¹ (44%) for BOD₇ and 0.05 mg·L⁻¹ (78% and 8%) for both TPt and TPs, as presented in Table 7 and Figure 5.

After MF, the BOD₇ concentration (16 mg·L⁻¹) in the microfiltration permeate remained stable, whereas the TPt and TPs were reduced further to <0.03 and 0.04 mg·L⁻¹ by precipitation with PACI (see Table 8); thus, that the rejections for both TPt and TPs were <1% (see Figure 5).

The initial water flux for the MFP-AIM membrane was 10.4 L·m⁻²·h⁻¹, and it decreased by 13% to a final value of 9.1 L·m⁻²·h⁻¹. The MFP-HTI water flux decreased by 15% from an initial value of 11.7 L·m⁻²·h⁻¹ to 9.9 L·m⁻²·h⁻¹. However, within the first 15 minutes of the MFP-HTI experiment, the water flux dropped to 10.4 L·m⁻²·h⁻¹ before decreasing steadily by 5% until achieving a final water flux of 9.9 L·m⁻²·h⁻¹, as shown in Figure 5. The FO permeate quality showed that the BOD₇ concentration was 3 times higher following the MFP-AIM membrane (14.5 mg·L⁻¹) in comparison to the MFP-HTI membrane (4.8 mg·L⁻¹). The TPt and TPs concentrations were below the quantification limit in both the MFP-AIM and MFP-HTI permeates (see Table 8). Previously, the AIM membrane has been shown to exhibit a higher rejection of small uncharged organic molecules compared to the HTI membrane [3,19]. Therefore, based on previous findings, the AIM membrane is expected to perform better than the HTI membrane if the rejection is due to size exclusion. Thus, it may seem surprising in this study that the HTI membrane exhibited the highest rejection. The better rejection of the HTI membrane in this case could be due to other effects, such as differences in the membrane charge leading to a difference in the rejection of charged molecules or a difference in the adsorption capability. If a larger amount of BOD can be adsorbed onto the HTI membrane, this could lead to a higher initial apparent rejection until saturation is reached. Finally, it is also possible that this single HTI result is an outlier because it is the only experiment in which the two membranes were found to deviate significantly.

Cationic flocculation

The addition of only cationic flocculant, which is also described as cationic polymer coagulation by Kvinnesland and Ødegaard [3942], leads to the binding of the negatively charged SS, creating macro-flocs. However, the cationic polymer does not precipitate soluble phosphorus (TPs), which is shown in Tables 9 and 10.

The MSF-AIM initial water flux was $10.2 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ and reached a final flux of $8.8 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ at the end of the experiment, corresponding to a decrease in the water flux of approximately 14%, as shown in Figure 6. The final concentrations in the MSF-AIM permeate were $20.8 \text{ mg}\cdot\text{L}^{-1}$ for BOD_7 and $0.1 \text{ mg}\cdot\text{L}^{-1}$ for TPt and TPs (see Table 9).

The MFP-AIM water flux declined by 35% from $13.7 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ to $8.9 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$, whereas the MFP-HTI declined by 2% from $13.2 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ to $12.9 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ (see Figure 6). The steep decline for the MFP-AIM membrane has been previously observed in a similar experiment with an identical setup (data not shown); therefore, membrane or system failure was disregarded. The duration of the MFP-HTI water flux assessment was 3.5 h instead of 4.5 h, which was caused by an abrupt stop in the electronic weight measurement and recording (see the vertical dotted line in Figure 6). Therefore, the average water fluxes of the MSF-AIM and MFP-AIM were adjusted to $9.0 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$, $10.6 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ and $12.7 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ for MSF-AIM, MFP-AIM, and MFP-HTI, respectively, for comparison.

The BOD_7 concentrations in the MFP-AIM and MFP-HTI permeates were $14.4 \text{ mg}\cdot\text{L}^{-1}$ and $15.1 \text{ mg}\cdot\text{L}^{-1}$, respectively. In comparison to the AIM results with coagulation and cationic flocculation, the AIM permeate quality was similar, indicating that coagulation does not affect the BOD_7 removal of the AIM membrane. For the HTI membrane, however, the permeate quality is now comparable to the AIM membrane, indicating that either the coagulation positively affects the HTI membrane and not the AIM membrane or that one of the results might be an outlier. Furthermore, the TPt and TPs concentrations found in both permeates were $0.05 \text{ mg}\cdot\text{L}^{-1}$ for the MFP-AIM and MFP-HTI membranes (see Table 10).

The addition of only cationic polymer was found to have less of an effect on the MSF-AIM water flux in comparison to MFP-AIM. This might be consistent with the formation of a protective layer by organic foulants, e.g., SS, which are caused by bacterial deposits on the MSF-AIM membrane surface [16]. Hence, the MSF-AIM membrane surface is less exposed to the possible remains of the cationic polymer and other cationic species (e.g., Ca, Fe, and Al) in comparison to the MFP-AIM membrane using a particle-free feed. This could explain the behaviours of the observed MSF-AIM water fluxes in the aforementioned experiments except for PACl with anionic polymer. Furthermore, because TFC membranes are often negatively charged, it is assumed that the AIM surface is more negatively charged than the HTI membrane (-32 mV at pH 7), thus having a higher fouling potential of cationic species [4043,4144].

Summary and discussion of the results

Aquaporin Inside™ with microsieve filtrate

Comparing all of the MSF-AIM results in Figure 7, only the PACl + anionic polymer pre-treatment experiment resulted in a higher water flux compared to the mechanical pre-treatment [16]. The pre-treatments with coagulation and/or flocculation resulted in slightly lower water flux values. In general, the water flux differences were very small and most likely within what can be expected from random fluctuations in the membrane performance and water quality. This means that regardless of the applied pre-treatment method, including microsieving, the fouling potential is unaffected (see Figure 7). The reason for this may be that the foulants are not sufficiently chemically affected by coagulation and/or flocculation to be completely removed by the microsieve. Thus, the foulants continue through the microsieve and can affect the membrane. Although the fouling potential is not significantly altered, a stable water flux was obtained with only a slight decline during several hours of operation. This is important for the rate at which membrane cleaning, e.g., CIP, will be necessary.

It is speculated that the created flocs passing through the microsieve can act as a protective (cake) layer, reducing the potential to interact with the membrane surface [444]. Regardless of the applied physicochemical pre-treatment method, the MSF-AIM permeate quality, i.e., BOD₇, did not improve in comparison to the mechanical pre-treatment, as shown in Table 11. However, the MSF-AIM permeates with only PACl and with PACl + anionic polymer satisfied the Swedish wastewater discharge demands for small and medium-sized WWTPs.

Aquaporin Inside™ with microfiltration permeate

The highest water fluxes were obtained for MFP-AIM ($12.0 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$) and MSF-AIM ($9.8 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$) when applying PACl+anionic polymer. The obtained MFP-AIM water flux was improved by 10% and by 20% upon applying only PACl ($11.0 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$) and PACl + anionic polymer ($12.0 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$), respectively, in comparison to the mechanical pre-treatment ($10.0 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$), which is shown in Figure 8. Furthermore, the MFP-AIM water flux with only cationic polymer obtained a 9% higher flux, although it declined linearly by 35%, reaching a zero water flux within 13 hours if extrapolated. The MFP-AIM permeate qualities were $3.4 \text{ mg}\cdot\text{L}^{-1}$ (PACl only) and $5.0 \text{ mg}\cdot\text{L}^{-1}$ (PACl + anionic polymer), and they were $\leq 0.06 \text{ mg}\cdot\text{L}^{-1}$ for TPT and TPs. In comparison to the mechanical pre-treatment, the MFP-AIM water flux was improved, although the BOD₇ concentrations in the permeates were 8 and 12 times higher. In addition, the BOD₇ concentrations in the permeates for the PACl + cationic polymer and cationic polymer were significantly higher, i.e., $16.8 \text{ mg}\cdot\text{L}^{-1}$ and $14.4 \text{ mg}\cdot\text{L}^{-1}$, respectively, in comparison to the concentrations with PACl only and PACl + anionic polymer. In conclusion, the MFP-AIM permeate with only PACl and PACl + anionic polymer were found to satisfy the Swedish wastewater discharge demand for small and medium-sized WWTPs.

HTI with microfiltration permeate

Physicochemical pre-treatment using PACl + anionic polymer on the MFP-HTI membrane improved the water flux by 19% ($13.4 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$) in comparison to the water flux with mechanical pre-treatment ($10.8 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$), which is shown in Figure 9. However, the BOD₇ concentration in the MFP-HTI permeate with PACl + anionic polymer ($4.7 \text{ mg}\cdot\text{L}^{-1}$) was 3.5 times higher than in the MFP-HTI permeate with mechanical pre-treatment ($1.5 \text{ mg}\cdot\text{L}^{-1}$), which is shown in Table 11. Furthermore, the

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use of cationic polymer on the MFP-HTI membrane increased the water flux by 15% to $12.7 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ and showed a water flux decrease of only 2% in comparison to the water flux with only mechanical pre-treatment, i.e., $10.8 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$, corresponding to a decrease of 36%. However, the BOD_7 concentrations with cationic polymer in the MFP-HTI permeate were 10 times higher in comparison to those with the mechanical pre-treatment and 3 times higher than those with PACI + anionic polymer. The permeate quality with PACI + cationic polymer was similar to the result with PACI + anionic polymer ($4.7 \text{ mg}\cdot\text{L}^{-1}$), which can be questioned because the BOD_7 concentration in all permeates (including AIM) involving the cationic polymer were at least 3 times higher than that with only PACI or PACI + anionic polymer.

Conclusions

The physicochemical pre-treatment of municipal wastewater in combination with forward osmosis can be applied with TFC AIM and HTI membranes for municipal wastewater treatment. This study showed that the addition of coagulant and/or flocculant can affect the water flux, water flux decrease and permeate concentration, i.e., BOD_7 , TPt and TPs. PACI and anionically charged and polyacrylamide-based flocculant in combination with microsieving and microfiltration achieved the highest water flux for both the MFP-AIM ($12.0 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$) and MFP-HTI ($13.4 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$) membranes compared to only mechanical pre-treatment ($10.0 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ and $10.8 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$, respectively). In addition, the same treatment configuration (PACI + anionic polymer) achieved the highest water flux with MSF as feed on the AIM membrane ($9.8 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$). The MFP-AIM and MFP-HTI permeates satisfied the Swedish discharge demands for small and medium-sized wastewater treatment plants regarding the BOD_7 , TPt and TPs concentrations in the permeate. The addition of only coagulant resulted in the lowest BOD_7 , TPt and TPs concentrations in the permeate. However, all tested physicochemical pre-treatment configurations exhibited at least double the BOD_7 concentration (range: 3.4 to $20.8 \text{ mg}\cdot\text{L}^{-1}$) in both the AIM and HTI permeates compared to only mechanical pre-treatment (range: 0.3 - $1.5 \text{ mg}\cdot\text{L}^{-1}$).

The addition of a physicochemical pre-treatment stage before FO requires higher capital costs but requires 20% less FO membrane area compared to mechanical pre-treatment. The operational and economic advantages and disadvantages need to be investigated.

Based on the findings of this study, in comparison with only mechanical pre-treatment, the physicochemical pre-treatment of municipal wastewater prior to FO can increase the water flux by up to 20%, although it does not improve the permeate quality of the investigated compounds, i.e., BOD_7 , TPt and TPs, because both the AIM and HTI membranes seem to perform well alone.

Acknowledgements

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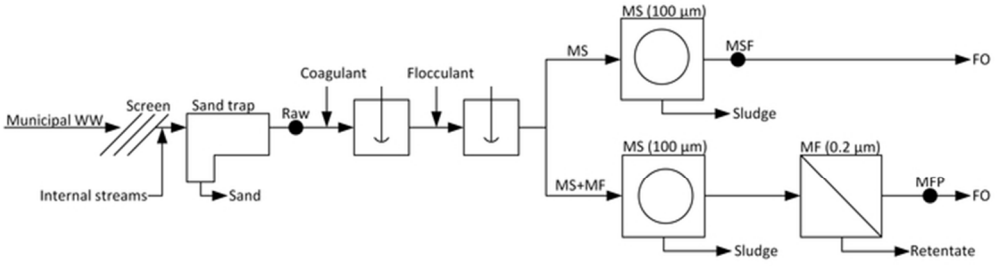


Figure 1. Process schematic of the pilot-scale plant, including coagulation and flocculation before microsieving (upper treatment path) and microsieving followed by microfiltration (lower treatment path). The black dots represent the sampling points during the experiment.

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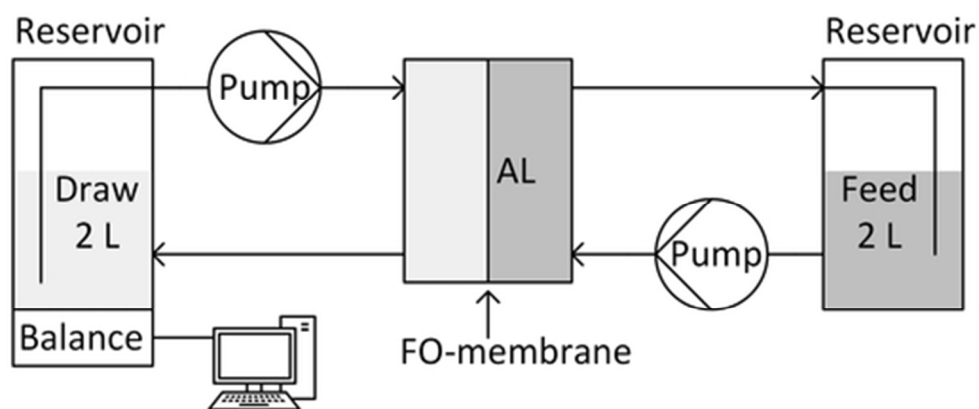


Figure 2. Schematic of the experimental FO setup.

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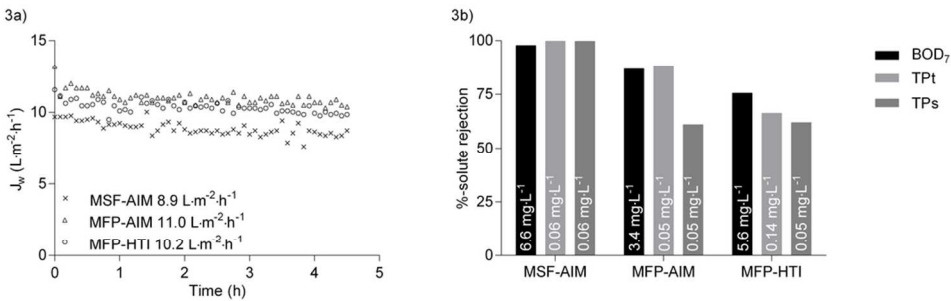


Figure 3. Average water flux J_w ($L \cdot m^{-2} \cdot h^{-1}$) as a function of time (h) for the AIM and HTI membranes with 15 $mg \cdot L^{-1}$ PACl as chemical pre-treatment (Figure 3a). The solute rejections (%) are displayed as bar graphs and corresponding concentrations in the FO permeates ($C_{Permeate}$, $mg \cdot L^{-1}$, displayed as numbers in the bar graph) of BOD₇, TPt and TPs with the MSF-AIM, MFP-AIM and MFP-HTI configurations (Figure 3b).

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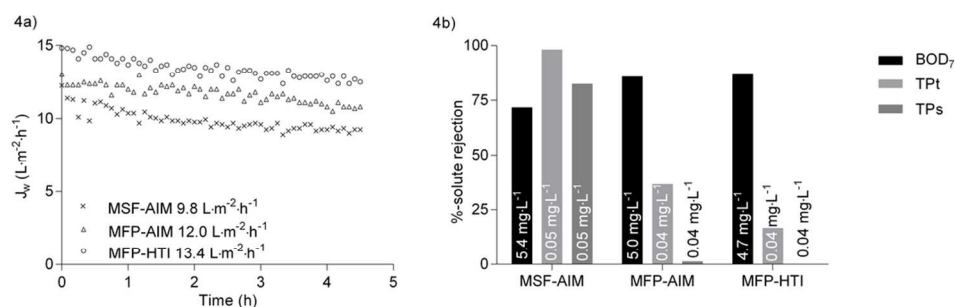


Figure 4. Average water flux J_w (L·m⁻²·h⁻¹) as a function of time (h) for the AIM and HTI membranes with 15 mg·L⁻¹ PACI and 3 mg·L⁻¹ anionic flocculant as chemical pre-treatment (Figure 4a). The solute rejections (%) are displayed as bar graphs and corresponding concentrations in the FO permeates (C_{Permeate}, mg·L⁻¹, displayed as numbers in the bar graph) of BOD₇, TPt and TPs with the MSF-AIM, MFP-AIM and MFP-HTI configurations (Figure 4b).

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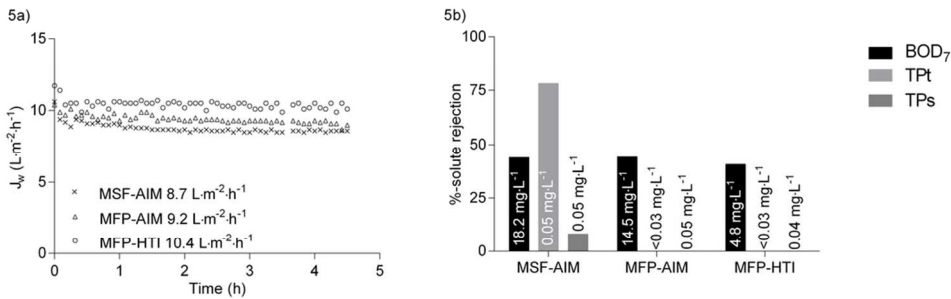


Figure 5. Average water flux J_w (L·m⁻²·h⁻¹) as a function of time (h) for the AIM and HTI membranes with 15 mg·L⁻¹ PACl and 4 mg·L⁻¹ cationic polymer as chemical pre-treatment (Figure 5a). The solute rejections (%) are displayed as bar graphs and corresponding concentrations in the FO permeates (C_{permeate}, mg·L⁻¹, displayed as numbers in the bar graph) of BOD₇, TPt and TPs with the MSF-AIM, MFP-AIM and MFP-HTI configurations (Figure 5b).

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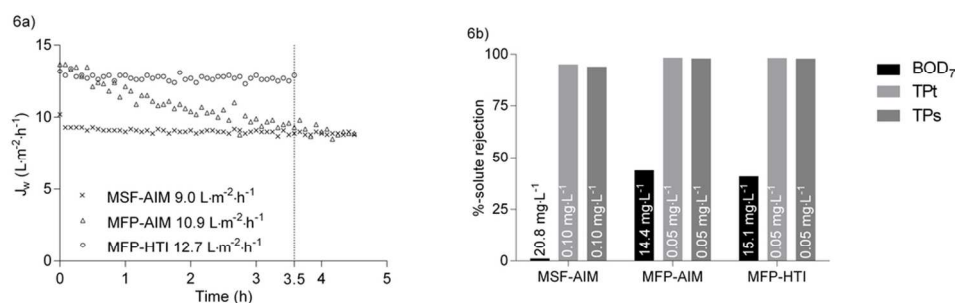


Figure 6. Average water flux J_w (L·m⁻²·h⁻¹) as a function of time (h) for the AIM and HTI membranes with only 4 mg·L⁻¹ cationic flocculant as chemical pre-treatment (Figure 6a). The solute rejections (%) are displayed as bar graphs and corresponding concentrations in the FO permeates (C_{Permeate}, mg·L⁻¹, displayed as numbers in the bar graph) of BOD₇, TPt and TPs with MSF-AIM, MFP-AIM and MFP-HTI configurations (Figure 6b).

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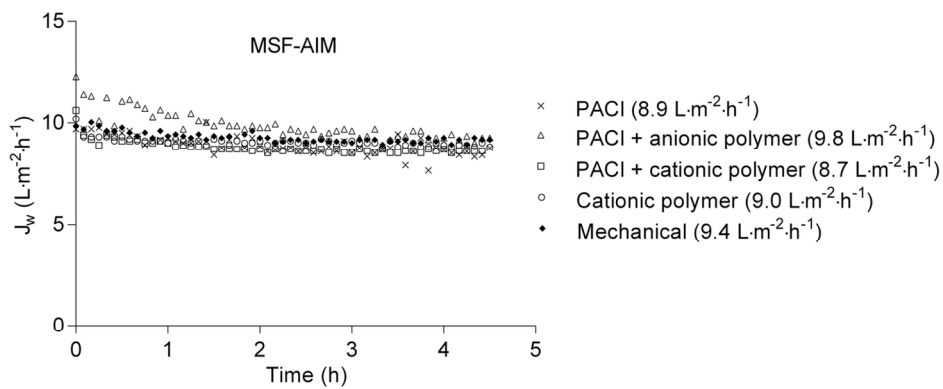


Figure 7. Summary of the average water fluxes (J_w , $L \cdot m^{-2} \cdot h^{-1}$) for the tested physicochemical (this study) and mechanical [16] pre-treatment methods of MSF-AIM as a function of time (h).

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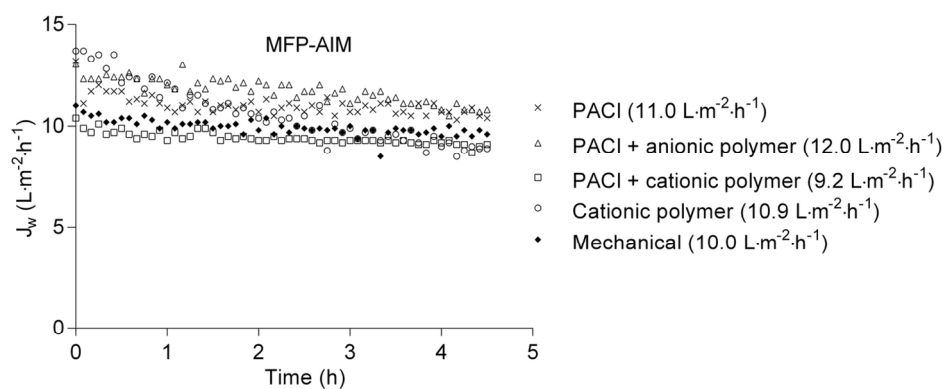


Figure 8. Summary of the average water fluxes (J_w , $L \cdot m^{-2} \cdot h^{-1}$) for the tested physicochemical (this study) and mechanical [16] pre-treatment methods of MFP-AIM as a function of time (h).

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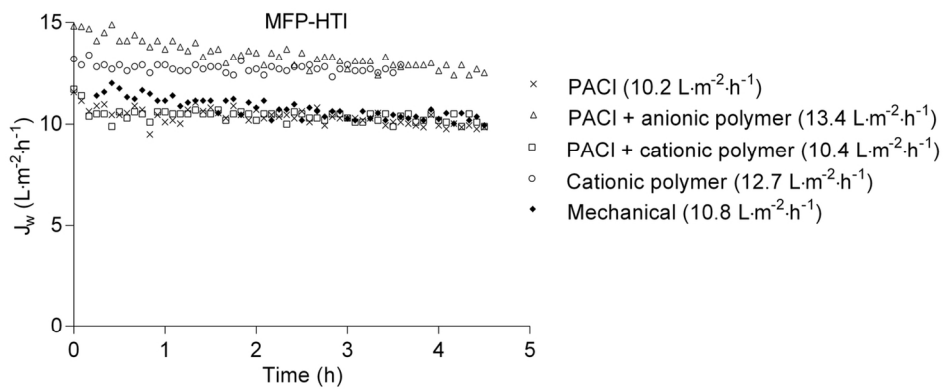


Figure 9. Summary of the average water fluxes (J_w , $L \cdot m^{-2} \cdot h^{-1}$) for the tested physicochemical (this study) and mechanical [16] pre-treatment methods of MFP-HTI as a function of time (h).

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Table 1. FO experiments with different physicochemically pre-treated feed solutions on AIM and HTI membranes. The FO draw solution was 2 M NaCl in all experiments.

FO membranes	Chemical treatment		Mechanical treatment	FO feed type
	Coagulant	Flocculant		
AIM	PACl		MS	MSF
AIM, HTI	PACl		MS+MF	MFP
AIM	PACl	Anionic	MS	MSF
AIM, HTI	PACl	Anionic	MS+MF	MFP
AIM	PACl	Cationic	MS	MSF
AIM, HTI	PACl	Cationic	MS+MF	MFP
AIM		Cationic	MS	MSF
AIM, HTI		Cationic	MS+MF	MFP

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Table 2. Wastewater characteristics of the feed to the pilot-scale plant at the sampling point (Raw).

	SS (mg·L ⁻¹)	BOD ₇ (mg·L ⁻¹)	TPt (mg·L ⁻¹)	TPs (mg·L ⁻¹)	pH (mg·L ⁻¹)
Avg. (n=8)	563	276	18.0	3.4	
Range (Min-Max)	240-975	120-630	6.7-36.0	1.8-6.8	7.2-7.5
Std.	270	158	11.2	1.6	

Table 3. Microsieve filtrate quality with the addition of only PACl.

	SS (mg·L ⁻¹)	BOD ₇ (mg·L ⁻¹)	TPt (mg·L ⁻¹)	TPs (mg·L ⁻¹)
Raw	680	290	20	3.3
Microsieve filtrate	630	230	18	0.09
MSF-AIM (Permeate)	0	6.6	0.06	0.06

Table 4. Microfiltration permeate quality with the addition of only PACl.

	SS (mg·L ⁻¹)	BOD ₇ (mg·L ⁻¹)	TPt (mg·L ⁻¹)	TPs (mg·L ⁻¹)
Raw	975	630	34	6.8
Microsieve filtrate	685	280	21	0.6
Microfiltration permeate	0	14	0.6	0.21
MFP-AIM		3.4	0.05	0.05
MFP-HTI		5.6	0.14	0.05

Table 5. Microsieve filtrate quality with the addition of PACl and anionic polymer.

	SS (mg·L ⁻¹)	BOD ₇ (mg·L ⁻¹)	TPt (mg·L ⁻¹)	TPs (mg·L ⁻¹)
Raw	975	280	36	3.4
Microsieve filtrate	35	13	1.9	0.16
MSF-AIM (Permeate)	0	5.4	0.05	0.05

Table 6. Microfiltration permeate quality with the addition of PACl and anionic flocculant.

	SS (mg·L ⁻¹)	BOD ₇ (mg·L ⁻¹)	TPt (mg·L ⁻¹)	TPs (mg·L ⁻¹)
Raw	490	370	14	4.7
Microsieve filtrate	7.2	59	0.41	0.18
Microfiltration permeate	0	28	0.04	0.04
MFP-AIM		5.0	0.04	0.04
MFP-HTI		4.7	0.04	0.04

Table 7. Microsieve filtrate quality with the addition of PACl and cationic polymer.

	SS (mg·L ⁻¹)	BOD ₇ (mg·L ⁻¹)	TPt (mg·L ⁻¹)	TPs (mg·L ⁻¹)
Raw	450	250	14	2.8
Microsieve filtrate	6.7	30	0.32	0.09
MSF-AIM (Permeate)		18.2	0.05	0.05

Table 8. Microfiltration permeate quality with the addition of PACl and cationic flocculant.

	SS (mg·L ⁻¹)	BOD ₇ (mg·L ⁻¹)	TPt (mg·L ⁻¹)	TPs (mg·L ⁻¹)
Raw	420	140	12	2.4
Microsieve filtrate	9.0	16	0.2	0.04
Microfiltration permeate	0	16	<0.03	0.04
MFP-AIM		14.5	<0.03	0.05
MFP-HTI		4.8	<0.03	0.04

Table 9. Microsieve filtrate permeate quality with the addition of only cationic flocculant.

	SS (mg·L ⁻¹)	BOD ₇ (mg·L ⁻¹)	TPt (mg·L ⁻¹)	TPs (mg·L ⁻¹)
Raw	270	130	7.4	1.8
Microsieve filtrate	9.8	14	1.8	1.6
MSF-AIM (Permeate)	0	20.8	0.1	0.1

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Table 10. Microfiltration permeate quality with the addition of only cationic flocculant.

	SS (mg·L ⁻¹)	BOD ₇ (mg·L ⁻¹)	TPt (mg·L ⁻¹)	TPs (mg·L ⁻¹)
Raw	240	120	6.7	1.8
Microsieve filtrate	12	19	2.1	1.6
Microfiltration permeate	0	14	1.8	1.4
MFP-AIM		14.4	0.05	0.05
MFP-HTI		15.1	0.05	0.05

Table 11. Overview of all conducted experiments with physicochemical and mechanical [16] pre-treated feed solutions on AIM and HTI membranes. The achieved water fluxes (J_W , $L \cdot m^{-2} \cdot h^{-1}$), water flux decrease ($J_{W,\%}$) and final BOD_7 , TPt and TPs concentrations ($mg \cdot L^{-1}$) in the permeate of the MSF-AIM, MFP-AIM and MFP-HTI membranes.

Chemical	Mechanical	AIM					HTI				
		J_W	$J_{W,\%}$	BOD_7	TPt	TPs	J_W	$J_{W,\%}$	BOD_7	TPt	TPs
PACl	MSF	8.9	10%	6.6	0.06	0.06	-	-	-	-	-
	MFP	11.0	13%	3.4	0.05	0.05	10.2	15%	5.6	0.14	0.05
PACl + anion polymer	MSF	9.8	24%	5.4	0.05	0.05	-	-	-	-	-
	MFP	12.0	17%	5.0	0.04	0.04	13.4	16%	4.7	0.04	0.04
PACl + cation polymer	MSF	8.7	19%	18.2	0.05	0.05	-	-	-	-	-
	MFP	9.2	13%	16.8	<0.03	<0.03	10.4	15%	4.8	<0.03	<0.03
Cationic poly.	MSF	9.0	14%	20.8	0.10	0.10	-	-	-	-	-
	MFP	10.9	35%	14.4	0.05	0.05	12.7	2%	15.1	0.05	0.05
Mechanical	MSF	9.4	7%	0.3	0.03	0.03	12.4	17%	1.5	0.10	0.04
	MFP	10.0	13%	0.4	0.04	0.04	10.8	36%	1.5	0.04	0.04

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Supplementary material

Table A. Water-flux decline, initial and final water-flux values of the AIM and HTI membrane.

Chemical	Mechanical	AIM			HTI		
		J _w ,%	Initial	Final	J _w ,%	Initial	Final
PACI only	MSF	10%	9.7	8.7	-		
	MFP	13%	12.0	10.4	15%	11.6	9.9
PACI + anionic polymer	MSF	24%	12.3	9.3	-		
	MFP	17%	13.0	10.8	16%	14.8	12.5
PACI + cationic polymer	MSF	19%	10.6	8.6	-		
	MFP	13%	10.4	9.1	5%	10.4	9.9
Cationic polymer only	MSF	14%	10.2	8.8	-		
	MFP	35%	13.7	8.9	2%	13.2	12.9
Mechanical	MSF	7%	9.9	9.2	17%	13.9	11.6
	MFP	13%	11.0	9.6	36%	15.4	9.9